Simulation and Sensitivity Analysis of Autothermal Reforming (ATR) for Mobile Fuel Cell Application

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Abstract

Autothermal Reforming (ATR) is one of the latest technologies for fuel reforming to produce hydrogen for fuel cell automotive application. ATR is a combination of an endothermic and exothermic process to give the maximum hydrogen productivity. It integrates the heat effect of the partial oxidation and steam reforming reactions by feeding the fuel, water and air or oxygen into the reactor. This process is carried out in the presence of a catalyst, which controls the reaction pathways and thereby determine the relative extents of oxidation and steam reforming reaction. In this paper, the development of ATR simulation model using MATLAB/SIMULINK environment is presented. Based on this model, the sensitivity analysis of the process is performed. The results of this study are discussed.

Keywords:

Autothermal reforming; hydrogen productivity; MATLAB/SIMULINK; sensitivity analysis.

Introduction

Fuel cell power system has received increased attention for transportation applications in recent years because of their potential for high efficiency and lower emissions [1-2]. Fuel cells are an electrochemical system that converts chemical energy directly into electricity by promoting a chemical reaction between two reactant gases. There are a variety of fuel cells systems for a different application is under development. These include proton-exchange membrane fuel cells (PEMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) [3]. Among these, PEMFC systems are being studied in this work.

PEMFC generates electric power from air and hydrogen or from a hydrogen-rich gas. Water and waste heat are the only by-products. Hydrogen–rich gas can be produced from conventional transportation fuels via various reforming technologies. There are three major reforming technologies which are Steam reforming (SR), partial oxidation (PO) and autothermal reforming, all consisting of similar steps. First, the fuel is vaporized. It is desired to maximize the hydrogen content while decreasing the carbon monoxide and methane formation. Then this gas mixture is further processed in the shift reactor. In this reactor, carbon monoxide is reacted with steam reforming to produce additional hydrogen by the water–gas shift reaction. The remaining carbon monoxide can be further converted into carbon dioxide by selection oxidation for hydrogen purification. The hydrogen-rich fuel containing carbon monoxide at below 10 ppm levels is ready to be fed [4].

Steam reforming shows the highest hydrogen production efficiencies. However, the required heat input due to endothermic reactions is considered as a major drawback for automotive applications. Partial oxidation needs external cooling. Autothermal reforming (ATR) promises better dynamic response comparing to these two reaction systems.

An ATR system is a coupling of endothermic and exothermic process to give the maximum hydrogen productivity. The autothermal reaction integrates the heat effect of the partial oxidation which is consisting of the sub-stoichiometric oxidation of methane, with steam reforming [5]. Under such conditions, the reaction mixture can be used as a heating/cooling medium and the reactor as a heat exchanger, all in one compact unit instead of a network of reactors and heat exchanger [6].

This study focused on numerical simulation of the ATR with steady state and dynamic model by using MATLAB/SIMULINK environment. Based on this model, the sensitivity analysis is performed to determine process constraints. In the ATR fuel processor, vaporized hydrocarbon fuel, oxygen and water (steam) are fed at controlled conditions to the reactor to produce the reformate gas mixture in an autothermal way. The reformate gas mixture containing the desired hydrogen

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must be processed further to convert carbon monoxide to carbon dioxide. The hydrogen-rich gas has to be cooled and humidified to desired fuel cell inlet conditions. The quality of the raw reformate (i.e. CH_4, O_2, CO, CO_2 and H_2O contents) is strongly affected by the reforming condition.

It should be noted that the concentration of the H_2 in the reformate influences the performance of the fuel cell stack. Higher hydrogen concentrations show better fuel cell performance. In general, CO content in the product hydrogen has to be below 10 ppm in order to be used as the anode gas for PEMFC [7]. In addition, if pure hydrogen is used in the feed stream, there is no power degradation of fuel cell stack and hence, increasing the life time of the fuel cell. Another advantage of using pure hydrogen is that fuel cell stack can run dead-end. It runs without the bleed-out of the anode gas from the stack, and hence maximizes the hydrogen utilization and minimizes the pressure loss in the stack due to the lower total gas flow through the stack. In line with these reasons, the use of hydrogen purifier downstream of the ATR system is desirable. However, a detailed hydrogen purification model is not part of this paper but is forthcoming.

Development of reactor model

Model assumption

In view of operation characteristic of the adiabatic fixed-bed reactor system for fuel cell application, the following assumptions are introduced:

1. Concentration and temperature gradients only occurs in the axial direction.
2. The catalyst particle is assumed to be isothermal and the main transport resistance inside the catalyst pellet is due to mass transfer, even in the case of highly exothermic reaction [8].
3. The transport mechanism in the axial direction is considered to be of the plug-flow type.

Mathematical model

A one-dimensional heterogeneous model is chosen in this work to simulate a tubular fixed-bed reactor. The mass and energy equations for the bulk and gas phase as well as the corresponding initial and boundary conditions are described below [8]:

Gas phase

$$\varphi_m \frac{d}{dz}\left(\frac{C_i}{\rho_f}\right) + k_g a_v \left(C_i - C_{i,s}^{*}\right) = 0 \quad (1)$$

$$\varphi_m c_p \frac{dT_g}{dz} + h_f a_v \left(T_g - T_s\right) = 0 \quad (2)$$

Solid phase

$$\rho_f \frac{1}{r_p^2}\frac{D_{e,i}}{\varepsilon^2}\frac{d}{d\varepsilon}\left(\varepsilon^2 \frac{d}{d\varepsilon}\left(\frac{C_{i,s}}{\rho_f}\right)\right) + R_{w,i}\rho_s = 0 \quad (3)$$

$$h_f a_v \left(T_g - T_s\right) + \left(1-\varepsilon_B\right)\Sigma_i\left(-\Delta_f H_i\right)\rho_s R_{w,i} = 0 \quad (4)$$

Gas-phase boundary conditions

$$z = 0 \qquad C_i = C_i^o, T_g = T_g^o \quad (5)$$

Solid-phase boundary conditions

$$\varepsilon = 0 \qquad \frac{d}{d\varepsilon}\left(\frac{C_{i,s}}{\rho_f}\right) = 0 \quad (6)$$

$$\varepsilon = 1 \qquad \rho_f \frac{D_{e,i}}{r_p}\frac{d}{d\varepsilon}\left(\frac{C_{i,s}}{\rho_f}\right)_{|\varepsilon=1} = k_g\left(C_i - C_{i,s}^{s}\right) \quad (7)$$

The simulation of the autothermal reaction is based on the following set of differential equations [9].

Continuity Equations

$$\frac{dx_{CH_4}}{dz} = \frac{\rho_b \Omega}{F_{CH_4}^o}\left(\eta_2 r_2 + \eta_3 r_3 + \eta_4 r_4\right) \quad (8)$$

$$\frac{dx_{O_2}}{dz} = \frac{\rho_b \Omega}{F_{O2}^o}\left(2\eta_2 r_2\right) \quad (9)$$

$$\frac{dx_{CO}}{dz} = \frac{\rho_b \Omega}{F_{CH_4}^o}\left(\eta_3 r_3 - \eta_5 r_5\right) \quad (10)$$

$$\frac{dx_{CO_2}}{dz} = \frac{\rho_b \Omega}{F_{CH_4}^o}\left(\eta_2 r_2 + \eta_4 r_4 + \eta_5 r_5\right) \quad (11)$$

Energy equation:

$$\frac{dT}{dz} = \frac{\rho_b}{u_s \rho_g C_p}\Sigma \eta_i r_i \left(-\Delta H\right)_i \quad (12)$$

For the pressure drop, the following equation is used:

$$\frac{dp_t}{dz} = -\frac{f\rho_g u_s^2}{d_p} \quad (13)$$

The effectiveness factors, η are taken from an average value based upon a number of off-line pellet simulations for the various effectiveness factors [9].

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Reaction kinetics

In the modelling of autothermal reforming of methane, it is necessary to combine all the rate equations for the total combustion, steam reforming and water gas shift reactions in the calculations. In this paper, the intrinsic reforming models proposed by Xu and Froment [10] are adopted as presented below. These authors derived the intrinsic rate equations for the steam reforming of methane on a $Ni/MgAl_2O_3$ catalyst.

Total oxidation

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \quad (14)$$

$$r_1 = \frac{k_{1a} p_{CH4} p_{O2}}{\left(1 + K_{CH4}^{ox} p_{CH4} + K_{O2}^{ox} p_{O2}\right)^2} + \frac{k_{1b} p_{CH4} p_{O2}}{\left(1 + K_{CH4}^{ox} p_{CH4} + K_{O2}^{ox} p_{O2}\right)} \quad (15)$$

Steam Reforming (CO production)

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (16)$$

$$r_2 = \frac{k_2^{xu} / p_{H2}^{2.5} \left(p_{CH4} p_{H2O} - p_{H2}^3 p_{CO} / K_{eq,3}\right)}{\left(1 + K_{CO} p_{CO} + K_{H2} p_{H2} + K_{CH4} p_{CH4} + K_{H2O} p_{H2O} / p_{H2}\right)^2} \quad (17)$$

Water-gas shift reaction

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (18)$$

$$r_3 = \frac{k_3^{xu} / p_{H2} \left(p_{CO} p_{H2O} - p_{H2} p_{CO2} / K_{eq,5}\right)}{\left(1 + K_{CO} p_{CO} + K_{H2} p_{H2} + K_{CH4} p_{CH4} + K_{H2O} p_{H2O} / p_{H2}\right)^2} \quad (19)$$

Steam Reforming (CO_2 production)

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \quad (20)$$

$$r_4 = \frac{k_4^{xu} / p_{H2}^{3.5} \left(p_{CH4} p_{H2O}^2 - p_{H2}^4 p_{CO2} / K_{eq,4}\right)}{\left(1 + K_{CO} p_{CO} + K_{H2} p_{H2} + K_{CH4} p_{CH4} + K_{H2O} p_{H2O} / p_{H2}\right)^2} \quad (21)$$

Simulation Studies

Following the development of the mathematical model of the system, simulation studies were implemented in MATLAB/SIMULINK environment. Sensitivity analyses were carried out to evaluate the influence of some key process variables on the overall system performance. The reactor was assumed adiabatic and the fuel gas mixture (Methane/steam/oxygen) is fed into the ATR at the selected T_{ATR}. The temperature of the exit product stream is determined by the extent of the endothermic and exothermic reaction in the reactor due to adiabatic conditions.

Results and Discussion

The reactor and catalyst dimensions, as well as operating conditions use to operate the fixed-bed reactor for hydrogen for fuel cells production is shown in Table 1. In this application, the reactor is operated at atmospheric pressure with methane and oxygen as a feedstock. Besides, water is added as reactant at the reactor inlet to increase hydrogen formation and to suppress coke deposition.

Table 1- Reactor dimensions, catalyst dimensions and operating conditions

Operating Conditions	Fuel Cell
Reactor	
Diameter of reactor, d_r (m)	0.4
Length of reactor, l_r (m)	0.5
Temperature (K)	830
Pressure, atm (P_{total})	1
Catalyst	
Catalyst used	$Ni/MgAl_2O_3$
Metal content (wt %)	15.2
Metal surface area (m^2g^{-1})	4.1
Density, ρ_s (kgm^{-3})	1870
Feed Composition	
CH_4/O_2	2.0
H_2O/CH_4	2.0
Oxygen sources	O_2

The parametric sensitivity of ATR behaviour and its performance have been investigated for several parameters including operating temperatures and kinetics parameter. The influence of these operational parameters on the product composition, i.e. product distribution, depends strongly on the thermodynamics of the reactions. For this purpose, analysis has been studied over the temperature range of 800–1015 K, feed flowrate from 1.0-3.0 m^3/s and steam to methane ratio 2.0-4.0. It has been found that the optimal operating temperature in ATR is 1015 K and feed flowrate of 2.0 m3/s and steam to methane ratio is 2.0-3.0.

The results are as follows:

1. Effect of temperature

Figure 1 shows that methane conversion at different feed temperatures. It indicates that methane conversion increases with increasing feed temperature. It reaches about 98.9% conversion at a temperature of 1015 K from 52.47% at 800 K. It has been found that after this value, a system becomes unstable.

2. Effect of step change in temperature on product distribution.

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Figure 2(a), clearly shows that the methane concentration is decreased when temperature is increased. This is due to the increase of the amount of available oxygen which enhances the exothermic reactions (CO_x formation). It has been noted that the CO concentration increases with temperature. When the temperature becomes larger than 900 K, high concentration of hydrogen is obtained as shown in figures 2(c) and 2(d). In contrary, figure 2(e) indicates that steam (H_2O) concentration is decreased when temperature is increased. This is because the higher the operating temperature, the more steam is needed for steam reforming reactions.

3. Effect of step change in feed flowrate on product distribution.

From the figure 3, the behaviour of product distributions, mainly concentration of CH_4, CO_2, H_2 and CO follows the pattern of the step change in temperature. At higher operating temperature, the oxygen is almost converted and it becomes unstable (negative value) as temperature above 1000 K and feed flowrate greater than 3.0 m^3/s were used (see figure 3(f))

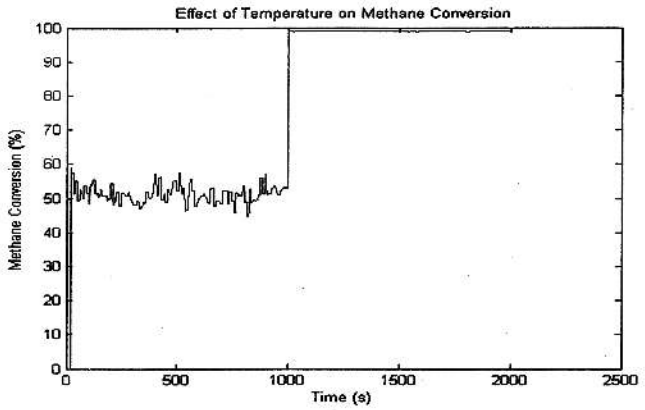
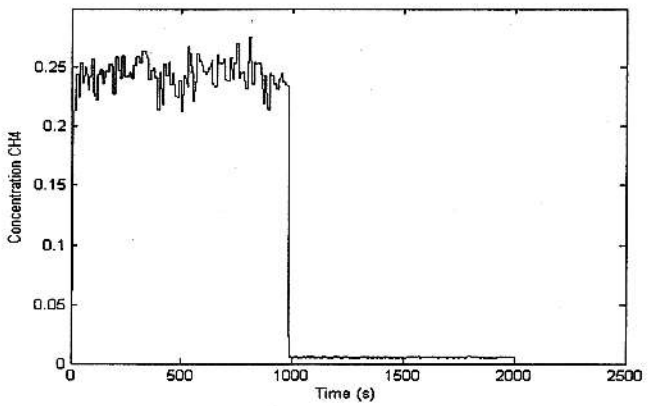
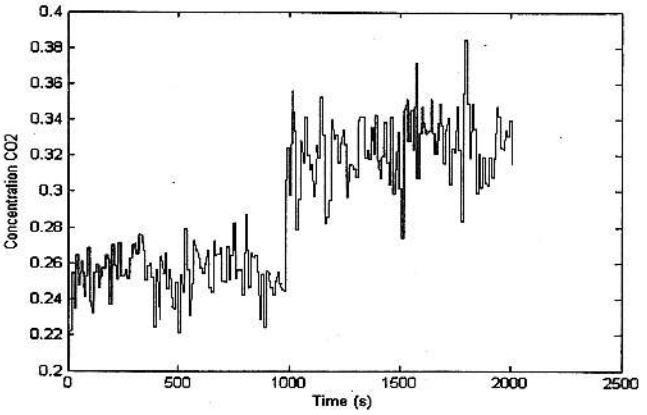


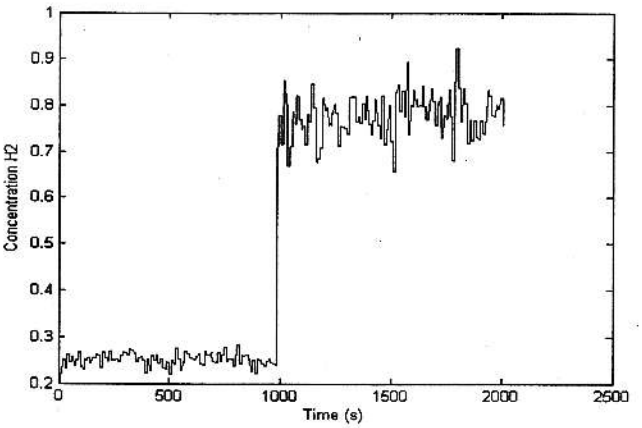
Figure 1 - Temperature profiles through the reactor with methane conversion.



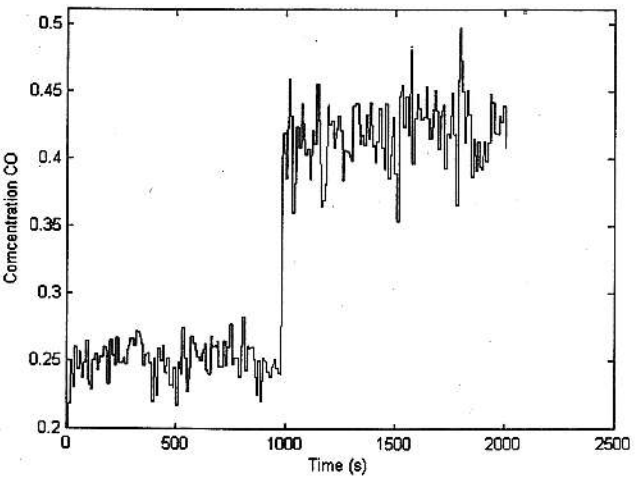
2(a)



2(b)



2(c)



2(d)

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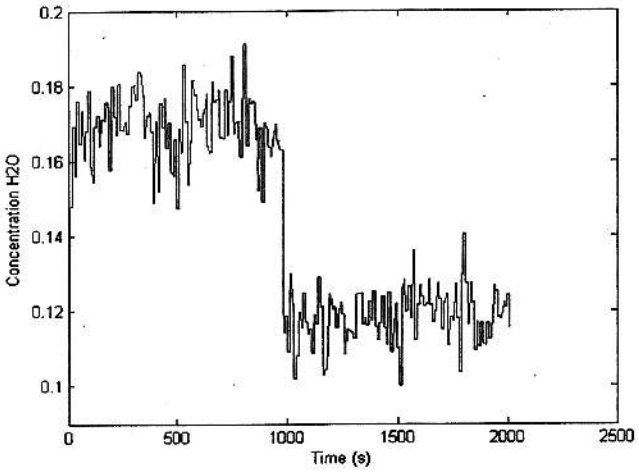
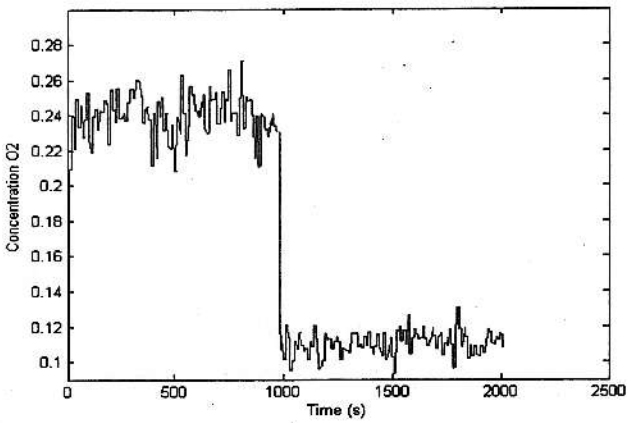
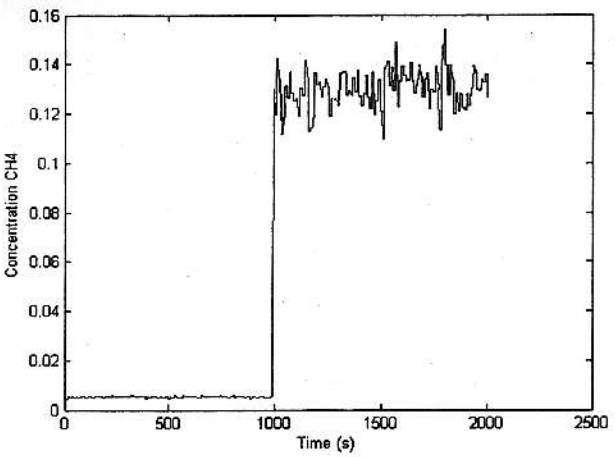


2(e)

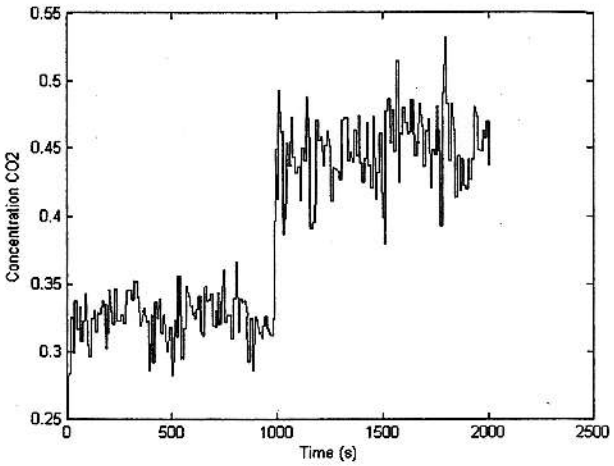


2(f)

Figure 2 - Effect of changing temperature on product distribution: (a) CH_4, (b) CO_2, (c) H_2, (d) CO, (e) H_2O, (f) O_2. Fix conditions: Feed flowrate 1 m^3/s, pressure 1 bar, and steam to methane ratio 2.0



3(a)



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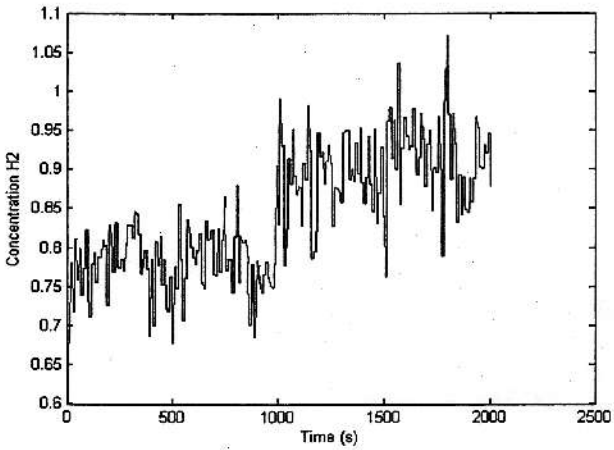

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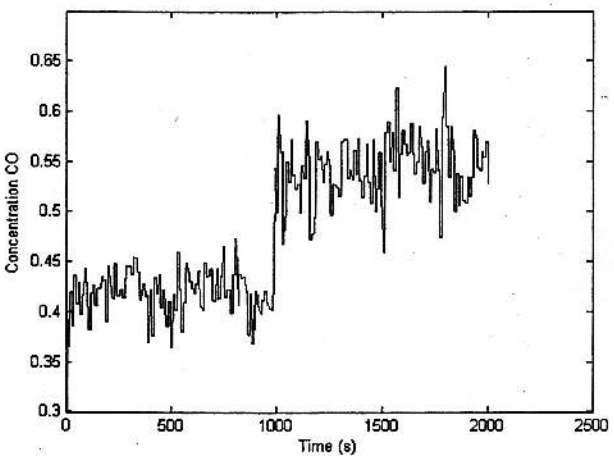

3(d)

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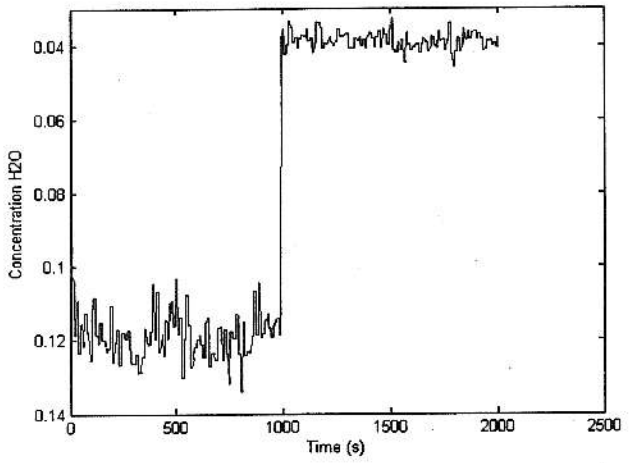
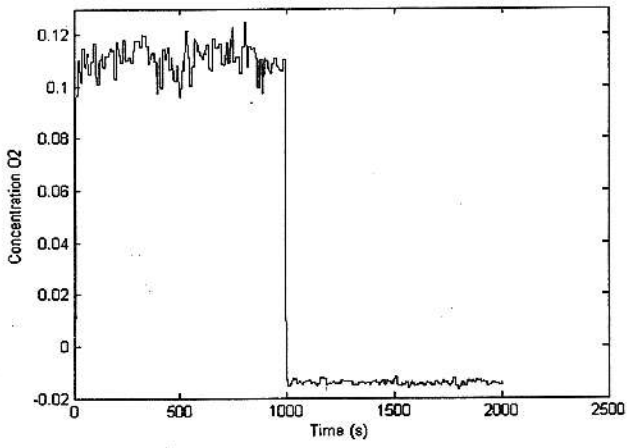


3(e)



3(f)

Figure 3 - Effect of changes of feed flowrate on product distribution. (a) CH_4, (b) CO_2, (c) H_2, (d) CO, (e) H_2O, (f) O_2. Fix conditions: Temperature 1015 K, pressure 1 bar, steam to methane ratio 2.0.

Conclusion

The kinetic model of Xu and Froment [10] for steam-methane reforming has been shown to be applicable to autothermal reactor operation. From the simulation results, temperature has a significant effect on hydrogen and carbon monoxide levels. At low temperature, methane may not be completely converted, even though the O_2/CH_4 ratio is greater than 0.5, resulting in lower H_2 and CO level. However at higher temperature the steam reforming reactions dominate and hydrogen and carbon monoxide level increase. It is also revealed that, the CO and H_2 formation is favoured at high temperatures and H_2 yield increasing at higher rate due to the water gas shift reaction and methane coupling reaction at higher temperature. Besides, higher methane conversion is obtained upon decreasing the feed flowrate and increasing temperature. From the thermodynamic analyses and kinetic simulation performed, the optimal operating conditions of the temperature <1015 K, H_2O/CH_4 ratio of 2.0-3.0, feed flowrate of 2.0 m^3/s and low pressure reforming is favorable due to the PEMFC is operate at atmospheric pressure.

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Nomenclature

φ_m superficial mass flow velocity, $kgm_r^{-2}s^{-1}$

a_v external pellet surface area per unit reactor volume, $m_i^2 m_r^{-3}$

A_i pre-exponential factor, reaction dependent

c_p specific heat at constant pressure, $J\ kg^{-1}\ K^{-1}$

C_i molar concentration of species *i*, mol m_g^{-3}

$C_{i,s}$ intra-particle molar concentration of species *i*, mol m_g^{-3}

$C_{i,s}^s$ molar concentration of species i, at the external pellet surface, mol m_g^{-3}

d_r reactor diameter, m_r

$D_{e,i}$ effective diffusion coefficient of species A in catalyst, $m_g\ m_i^{-2}s^{-1}$

h_f gas-to-solid heat transfer coefficient, $W\ m_i^{-2}\ K^{-1}$

k_g gas-to-solid mass transfer coefficient, $mg^3\ m_i^{-2}s^{-1}$

k_i reaction rate constant of reaction *i*

K_{eqi} equilibrium constant of reaction i

K_i adsorption constant for component *i*, bar^{-1}

K_i^{ox} adsorption constant for component *i*, in combustion reaction, bar^{-1}

l_r reactor length, m

p_i partial pressure of component *i*, bar

P_{tot} total pressure, bar

r_i rate of reaction i, mol $kg_{cat}^{-1}s^{-1}$

r_p pellet radius, m

$R_{w,i}$ net catalytic production rate of species *i*, per unit catalyst mass, mol $kg_{cat}^{-1}s^{-1}$

T_g gas-phase temperature, K

T_s solid temperature, K

z axial reactor co-ordinate, m

ΔH_i^o standard adsorption enthalpy, $J\ mol^{-1}$

$-\Delta_f H_i$ heat of formation of species *i*, $J\ mol^{-1}$

ε_B void fraction of packing, $m_g\ m_r^{-3}$

ζ dimensionless pellet co-ordinate

ρ_f fluid density, kg m_g^{-3}

ρ_g gas density, kg m_g^{-3}

η_i effectiveness factor for reaction *i*.

Ω cross sectional of reactor, m^2

x_{CH_4} conversion of methane (%)

x_{CO_2} conversion of methane to CO_2 (%)

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